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SEVENTH INTERNATIONAL SUMMER INSTITUTE IN SURFACE
SCIENCE(U) WISCONSIN UNIV-MILWAUKEE DEPT OF CHEMISTRY
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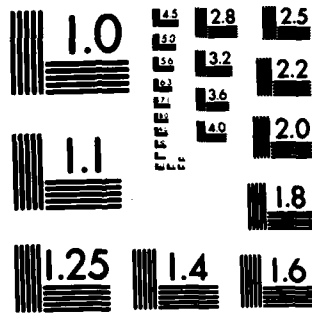
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9. ABSTRACT (Continue on reverse if necessary and identify by block number) At the Seventh International Summer Institute in Surface Science, twenty-one leading scientists presented tutorial review lectures on gas/solid interfaces. Paper topics: "Surface Structure Analysis by Low Energy Alkali Ion Scattering"; "Scanning Tunneling Microscopy-A Critical Review"; "Georg-Maria Schwab: Early Endeavours in the Science of Catalysis"; "Raman Spectroscopy of Adsorbed Molecules"; "Inverse Photoemission Spectroscopy"; "Multilayer Films-Wetting Behavior"; "Molecular Organometallic Chemistry and Catalysis on Metal-Oxide Surfaces"; "Effects of Promoters and Poisons on Surface Reactions"; "Thermodynamics and Kinetics in Weakly Chemisorbed Phases"; "The Life and Times of Paul H. Emmett"; "Catalysis by Molybdena Alumina and Related Systems"; (Cont. on reverse side of page 0)			
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- ↗ "Surface Electronic States";
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- "Stable Intermediates on Transition Metal Surfaces";
- "Field Emission Microscopy - Trends and Perspectives";
- "Wetting - An Experimenter's View";
- "Catalysis by Metals";
- "High Resolution Electron Microscopy in Surface Science";
- ↗ "Structure and Catalytic Performance of Zeolites";
- ↗ "Elastic and Inelastic Electron Scattering for Surfaces";
- ↗ "Time-of-Flight Atom-Probe Studies of Gas-Surface Interactions";
- "Kinetic and Spectroscopic Investigations of Surface Chemical Processes".

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SEVENTH INTERNATIONAL SUMMER INSTITUTE IN SURFACE SCIENCE
(ISSS 1985)

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The academic goals of ISISS were outlined in the editorial comments of "Surface Science: Recent Progress and Perspectives (ISISS 1975)":

"The favorable acceptance of ISISS was gratifying, but did not exactly come as a surprise. During the recent decade, advanced ultrahigh vacuum technology has made the achievement of pressures $< 10^{-10}$ Torr a routine operation so that surfaces, once freed from impurities, can be kept clean over a sufficient length of time and adsorbates then can be admitted at well-dosed amounts. Techniques for surface analysis were more and more refined; with the atom probe we are now able to analyze even single surface atoms or chemical complexes. Progress in the theory of the solid state subsequently allowed some fruitful dealing with the theoretical aspects of solid surfaces. All these developments combined with the demand for data by vital branches of our modern technology, caused an increasing flood of publications especially in the field of gas-solid interfaces. It became hard to catch up with the literature in one's own narrow area and it appeared nearly impossible to keep track of the developments in neighboring fields. As in other fast developing parts of the natural sciences, one consequently observes some isolationism and the appearance of communication problems. It is quite clear that such a tendency, where one no longer learns from progress or setbacks in neighboring areas, would be very much to our disadvantage. To counteract this tendency, ISISS was organized. Leading experts from various subdivisions of surface science - we chose to restrict the topics to gas-solid interfaces - presented tutorial review talks in which recent progress was summarized and future trends were pointed out."

In order to keep ISISS 1985 at a level of highest quality, all former ISISS speakers were invited to suggest names of suitable lecturers. To avoid duplication, none of the lecturers of the 1983 Summer Institute were invited to present a paper. The final list showed twenty-one internationally known experts in the field of gas-solid interfaces. The speakers came from Germany, the United Kingdom, and from the U.S.A.

The following list shows their names, their affiliations, topics, and short summaries of the papers presented.

E. Bauer, Technische Universität Clausthal, Germany

Surface Structure Analysis by Low Energy Alkali Ion Scattering

After a brief outline of low energy ion scattering in general, the advantages of alkali ions relative to noble gas ions will be discussed. Then the basic phenomena which occur in alkali ion scattering will be illustrated for a clean unreconstructed surface ($W\{110\}$). This will be followed by a discussion of studies of more complex surfaces such as reconstructed surfaces (e.g. $Au\{110\}$) and of chemisorption layers. An attempt will be made to review critically all work done up to now and to indicate expected future developments.

R. J. Behm, Universität München, Germany

Scanning Tunneling Microscopy--A Critical Review

1. Introduction
2. Experimental Considerations
3. Tunnel Current and Tunnel Barrier
 - 3.1 Basic Model Calculations and Approximations
 - 3.2 Calculations for Nonplanar Tip-Surface Geometries
 - 3.3 The Effect of the Image Potential
 - 3.4 Resolution of the SIM
 - 3.5 Sample Conductivity
 - 3.6 Effect of Adsorbates
4. Surface Microscopy
 - 4.1 Topography of Flat Surfaces
 - 4.2 Periodic Structures of Single-Crystalline Surfaces
 - 4.3 Surface Defects
 - 4.4 Reactivity and Stability of Surfaces
 - 4.5 Non-surface-science Application of the SIM
 - 4.6 Surface Diffusion and Surface Mobility
5. Tunneling Spectroscopy
 - 5.1 Valence Band Spectroscopy
 - 5.2 Resonant Tunneling
 - 5.3 Scanning Tunneling Spectroscopy
 - 5.4 The Work Function and Work Function Images
6. Conclusion

J. H. Block, Fritz-Haber-Institut, Berlin, Germany

Georg-Maria Schwab: Early Endeavours in the Science of Catalysis

A. Campion, University of Texas at Austin, Texas

Raman Spectroscopy of Adsorbed Molecules

I will describe recent experiments that demonstrate our ability to observe Raman scattering from molecules adsorbed on single crystal surfaces without requiring either surface or resonance enhancement. I will discuss the details of the experimental method, relevant selection rules, information obtainable from the angular distribution of the scattered radiation and some implications of our experiments regarding the mechanism of surface-enhanced Raman scattering. To illustrate the versatility of our method, examples will include studies of molecules adsorbed on metal, semiconductor and dielectric surfaces in ultrahigh vacuum, in the presence of reactive gases at high pressure and in the electrochemical environment.

V. Dose, Universität Würzburg, Germany

Inverse Photoemission Spectroscopy

- I. Introduction: History
basic concepts
- II. Experimental instrumentation: Energy selective Geiger counter
grating spectrographs
chromatic imaging of lenses
- III. Bulk electronic states
unoccupied states in copper
mapping of dispersion relations
absolute k-space location by energy coincidence
temperature effects
- IV. Surface electronic states
multiple reflection model
image potential states
crystal derived empty states
- V. Adsorbate induced states
oxygen adsorbed on nickel
CO and NO adsorption on Pd
CO adsorption on potassium promoted Pt { 111}
- VI. Summary and outlook

C. Ebner, Ohio State University, Ohio

Multilayer Films - Wetting Behavior

- I. Introduction
 - A. Wetting and non-wetting behavior
 - 1. First-order transitions (pre-wetting transition)
 - 2. Continuous or critical transitions
 - 3. Dependence on potentials
 - 4. Experimental observations

- II. Theoretical Approaches
 - A. Landau theory
 - B. Lattice models
 - C. Continuum theories
- III. Some Applications of the Theory
 - A. Potential strengths and the existence of wetting transitions
 - B. Potential ranges and the order of the wetting transitions
 - 1. Critical exponents
 - 2. "Tuning" the potential
 - C. Wetting by solid films
 - 1. Layering transitions and roughening
 - 2. Epitaxy
 - D. Triple point wetting
- IV. Future trends
 - A. Adsorbates of non-spherical molecules
 - B. Kinetics of wetting
 - C. Other
- V. Summary

B. C. Gates, University of Delaware, Newark

Molecular Organometallic Chemistry and Catalysis on Metal-Oxide Surfaces

- I. Introduction: the complexity of traditional supported metal catalysts and the motivation for preparation of supported "molecular" structures
- II. Preparation of "molecular" organometallics (carbonyls of Fe, Ru, Os, Re, and Rh) on surfaces of metal oxides (γ - Al_2O_3 , SiO_2 , and MgO)
- III. Characterization by physical methods
 - A. Vibrational spectra: infrared, Raman, and IETS
 - B. Electronic spectra
 - C. EXAFS
 - D. High-resolution transmission electron microscopy
- IV. Reactivity
 - A. Destruction of "molecular" organometallics and formation of cationic complexes and metal crystallites
 - B. Stabilization of anionic complexes and clusters on basic supports (MgO)
- V. Catalysis by supported "molecular" clusters
 - A. Low-temperature reactions of olefins
 - B. High-temperature reaction of $\text{CO} + \text{H}_2$

VI. Catalysis by structurally simple supported metals derived from surface organometallic precursors

VII. Summary and prospects: new classes of catalysts

D. W. Goodman, Sandia National Laboratory, New Mexico

Effects of Promoters and Poisons on Surface Reactions

Recent work has demonstrated the special advantages in fundamental catalytic studies of combining in a single apparatus the ability to measure reaction kinetics at elevated pressures with the availability of modern surface analytical techniques. This approach has shown that low surface area single crystals can be used successfully to model several important catalytic systems including CO and CO₂ methanation, olefin hydrogenation, and CO oxidation. Virtually identical kinetic parameters have been found for these reactions over single crystals of nickel, ruthenium, and rhodium as are observed for the corresponding supported catalysts. Using surface analytical techniques to monitor quantity and ordering of impurity atoms (e.g., S, P, Ag, Cu, K) on catalytically active substrates, a correlation has been found between the electronegativity of the impurity atom and its influence on reactivity. These results are consistent with electronic or ligand effects playing a major role in the modification of catalytic properties by surface impurities. These results will be discussed in the context of their relevance to more realistic supported catalyst systems.

M. Grunze, University of Maine, Orono

Thermodynamics and Kinetics in Weakly Chemisorbed Phases

In this lecture we will discuss the thermodynamic and kinetic behavior of weakly chemisorbed phases and summarize what has been reported in the literature and unpublished data from our laboratory on the correlation between thermodynamic and kinetic behaviour. The adsorption system to be discussed include, for example, CO/Ru{0001}, CO/Cu{110}, N₂/Ni{110}, and N₂/Ni{100}. In this lecture, we will review the experimental techniques and data evaluation procedures to determine thermodynamic and kinetic quantities and their correlation using transition state theory and detailed balancing arguments. The feasibility to use low energy ion scattering experiments (ISS) to determine thermodynamic quantities at extremely low surface coverages ($\sim 10^{-3}$ of a monolayer) will be demonstrated and some recent results on the spectroscopic identification of "precursor" states will be presented.

W. K. Hall, University of Wisconsin-Milwaukee, Wisconsin

The Life and Times of Paul H. Emmett

W. K. Hall, University of Wisconsin-Milwaukee, Wisconsin

Catalysis by Molybdena Alumina and Related Systems

Molybdena-aluminas are good hydrogenation catalysts which are not poisoned by sulfur; they are most widely used for hydrodesulfurization of oils. They are, however, multifunctional. Under appropriate conditions they may catalyze hydrogenation of olefins, diolefins and aromatics as well as olefin metathesis and geometric isomerizations. The latter have been attributed to acid catalysis. The goal of our research is to understand the elements of this chemistry on the molecular level.

One approach has been to characterize the sites which are effective for these reactions. These were counted by selective poisoning experiments and found to amount to no more than a few per cent of total molybdenum atoms present. One such poison was NO, which adsorbed exclusively as a dinitrosyl species. Thus, a high degree of coordinative unsaturation was demonstrated and a lower valence state suggested for the molybdenum atoms at these centers than required by the bulk composition. For example, the sites may contain Mo⁺² or Mo⁺³ ions, when Mo⁺⁴ are expected. Evidence has been collected showing that lower valence states are indeed present and that it is likely that they are Mo²⁺ ions. The dissociative adsorption of H₂ was also poisoned by selectively chemisorbed NO or O₂. Interestingly, the H₂ atoms formed at these centers become delocalized; they may travel and perhaps react at sites remote from the dissociation centers. ¹H-NMR studies of H₂ adsorbed at 78K together with experiments utilizing D₂ have clearly identified the sites where dissociation occurs with those necessary for hydrogenation.

Studies of the reactions of olefins with D₂ were made. Presently, attention will be focused on the reactions with ²1-4 butadiene since they clearly define both the extent and limitations of our knowledge. The reaction scheme is definite but the origins of selectivity factors remain to be defined. Moreover, the site requirements for olefin metathesis and cyclopropane isomerization remain unclear. These reactions would seemingly have the same site requirements as for hydrogenation, but they respond differently to poisoning molecules. Moreover, it has been found that reactions have been termed "acid catalyzed" have a different chemistry.

F. J. Himpsel, IBM T.J. Watson Research Center, Yorktown Heights, New York

Surface Electronic States

Electronic states determine important properties of surfaces and interfaces, e.g., the bonding, the reactivity with adsorbates, the Fermi level pinning position and Schottky barrier height.

Photoemission and inverse photoemission (or bremsstrahlung spectroscopy) are shown to be complementary techniques for probing occupied and unoccupied electronic states, respectively. The momentum of delocalized valence states can be measured as well as their energy if low electron (photon) energies in the 10-40 eV range are used. Thus, energy band dispersions are obtained for bulk, surface, and adsorbate states which cannot be determined by other techniques.

For complex surfaces and interfaces the core states are best suited to extract the maximum amount of information about the electronic structure and the chemical bonding (e.g. the oxidation state). Using synchrotron radiation one obtains the surface sensitivity and energy resolution that is needed to resolve chemical shifts at surfaces.

Applications towards the understanding of the Si-SiO₂ interface and the dry etching process are given.

J. Kirschner, Institut für Grenzflächenforschung und Vakuumphysik, Jülich, Germany

Use of Spin-polarized Electrons in Surface Analysis

The use of polarized electrons for the structural, electronic and magnetic analysis of surfaces is demonstrated. Examples are: contraction and thermal expansion at the W{100} surface, symmetry-resolved bandstructure of Pt{111} via spinpolarized photoemission, surface magnetism of clean and adsorbate covered Fe surfaces, magnetic single-particle excitations in Ni and the unoccupied exchange-split bandstructure of Fe.

R. J. Madix, Stanford University, California

Stable Intermediates on Transition Metal Surfaces

Several metals are used as catalysts for heterogeneous oxidation processes. In this talk studies of oxidation reactions on Group II B metals will be discussed with particular emphasis on the identification of the chemical nature and structure of intermediates on single crystal surfaces. Examples to be included are SO₂, CH₃CN, HCOOH and CH₃OH. The tools used for structural determination are vibrational spectroscopy and X-ray absorption fine structure.

A. J. Melmed, National Bureau of Standards, Gaithersburg, Maryland

Field Emission Microscopy - Trends and Perspectives

I. Introduction

- A. Brief discourse on curved and flat surfaces
- B. Limits of this talk - FEM, FIM in surface science
- C. Historical outline

- II. Field Electron Microscopy
 - A. Description
 - B. Selected achievements
- III. Field Ion Microscopy
 - A. Description
 - B. Selected achievements
- IV. Future Outlook (Perspectives)

L. Passell, Brookhaven National Laboratory, Upton, New York

Wetting - An Experimenter's View

Review of neutron and x-ray scattering studies of the phases formed by ethylene films on graphite basal plane surfaces in various coverage and temperature regimes and of the wetting transitions which occur in these films. Also discussed will be the effect on these wetting transitions of preplating the graphite surfaces with a monolayer of xenon.

J. Sinfeldt, Exxon Research and Engineering Co., Annandale, New Jersey

Catalysis by Metals

The area of catalysis by metals is technologically very important and also provides good illustrations of basic concepts in catalysis. In one form of metal catalyst which is widely used commercially, the catalyst particles consist of a porous refractory material with small metal crystallites or clusters dispersed throughout the particles. The refractory material is frequently an oxide such as alumina or silica. In some cases virtually all of the atoms in the metal clusters are surface atoms.

The refractory material is commonly known as a carrier or support. In some cases it contributes a catalytic function of its own, distinct from the catalytic function associated with the metal. The phenomenon of bifunctional catalysis then occurs. The sites on the metal clusters catalyze one type of step in a reaction sequence, while sites on the carrier catalyze another. In a common example involving hydrocarbon reactions, metal sites catalyze hydrogenation-dehydrogenation steps while acid sites on the carrier catalyze olefin isomerization steps.

During the past 15 years, bimetallic systems have attracted much attention as catalysts. Dramatic selectivity effects are frequently observed with such materials. Highly dispersed catalyst entities known as "bimetallic clusters" have been investigated extensively, since they have found widespread application in petroleum reforming processes. The characterization of these clusters with the use of chemical and physical probes has provided an exciting challenge for the catalytic scientist.

D. J. Smith, Arizona State University, Tempe, Arizona

High Resolution Electron Microscopy in Surface Science

Recent improvements to high resolution electron microscopes have made it possible to image surfaces on the sub-nanometre scale using a reflection imaging mode and on the atomic scale using the transmission and surface profile imaging modes. The first part of the lecture will describe these various techniques, in particular discussing their various advantages and shortcomings with respect to surface imaging. The bulk of the lecture will concentrate on reviewing the results now starting to appear which include direct observation of atomic (re)arrangements on extended gold surfaces and on small oxide and metal particles. The correlation with traditional "bulk" characterization methods will be discussed and, finally, likely future developments will be summarized.

J. M. Thomas, University of Cambridge, United Kingdom

Structure and catalytic Performance of Zeolites

Zeolites are used extensively as industrial and laboratory catalysts: faujasitic solids (zeolite-Y and mordenite) are the corner-stone of the catalytic cracking and hydrocracking of gas oil; porotectosilicates (zeolite ZSM-5 and ZSM-11) are employed both for the conversion of methanol to petrol (gasoline) and for the shape-selective alkylation of benzene by ethylene to monoethylbenzene. Many other zeolites are under development for the catalytic utilization of synthesis gas, saturated hydrocarbons and heavy oils. Already there are well over a hundred distinct, known types of zeolites, but their structural details can only rarely be elucidated by conventional X-ray-based methods. Good progress has, however, been achieved in correlating the performance of zeolite catalysts with the structural characteristics that have been retrieved by the combined use of solid-state NMR, neutron and X-ray (powder) methods, computer modelling and high-resolution electron microscopy. The last named technique is especially useful in imaging (in projection) the structure of the entire solid catalyst; and the neutron (and X-ray) Rietveld method reveals the nature of the active site implicated in the catalytic action of the appropriately cation-exchanged zeolite. The lecture will illustrate how the hitherto unknown structures of certain zeolite catalysts have been solved, and the abnormal features of zeolites of known structures have been clarified by the application of the above-mentioned techniques.

S. Y. Tong, University of Wisconsin-Milwaukee, Wisconsin

Elastic and Inelastic Electron Scattering for Surfaces

In this talk, we shall review the use of elastic and inelastic electron scattering processes for the study of surface structure. For elastic electron scattering, we shall review the technique: Low-Energy Electron Diffraction, LEED. For inelastic electron scattering, we shall present new results of High-Resolution Electron Energy Low Spectroscopy (HR-EELS). Clean metal surfaces, semiconductor surfaces and adsorbate covered metal surfaces will be covered.

T. T. Tsong, The Pennsylvania State University, University Park

Time-of Flight Atom-Probe Studies of Gas-Surface Interactions

In field ion microscopy, the surface of a sharp emitter can be imaged with atomic resolution and surface atoms of one's choice can be field desorbed and be identified one by one using the time-of-flight atom-probe. The composition depth profiles of alloys in surface segregation can be derived with true single atomic layer depth resolution. With the introduction of the pulsed-laser technique to the atom-probe operation, and the development of the high resolution pulsed-laser atom-probe and the pulsed-laser imaging atom-probe, gas surface interactions and surface catalyzed simple chemical reactions can now be studied. Atomic rearrangements of the substrate by chemisorption and the desorption sites of the reaction products can be revealed from the field ion image and the field desorption image. Reaction intermediates can be identified from the pulsed-laser stimulated field desorption mass spectrum. Desorption of multiatomic clusters and their magic numbers, and the critical numbers of multiply charged ions can also be studied. Very fast ion reactions of reaction time in the 10^{-13} to 10^{-15} sec range can be studied with a time resolution of 10 to 20 femtoseconds (10^{-15} sec). Those ToF atom-probe FIM studies aimed to elucidate detailed atomic steps in catalytical reactions on solid surfaces and gas-surface interactions will be discussed.

J. T. Yates, Jr., University of Pittsburgh, Pennsylvania

Kinetic and Spectroscopic Investigations of Surface Chemical Processes

Understanding the detailed behavior of organic molecules as they interact with metal surfaces is of fundamental importance in surface chemistry. Two basic methods may be employed to obtain information about the surface chemistry of molecules - kinetic studies of product evolution and reactant consumption, and spectroscopic studies of surface species. In this talk, a new rapid kinetic method, scanning kinetic spectroscopy (SKS), will be discussed. It will be shown how SKS may be used to rapidly discriminate reaction channels which open as temperature and surface coverages change. The use of the deuterium kinetic isotope effect (DKIE) provides deep insight into the nature of the surface elementary steps at work. In addition, the power of transmission IR spectroscopy to study interesting surface species and their behavior will be illustrated for organic processes on small supported metal clusters.

Since the discussions are an essential part of ISISS, the Session Chairmen play an important role. At ISISS 1985, the following surface scientists served as Chairmen:

Professor Bruce Tatarchuk
Dept. of Chemical Engineering
Auburn University
Auburn, Alabama 36849

Professor David Lichtman
Laboratory for Surface Studies
University of Wisconsin-Milwaukee
Milwaukee, WI 53201

Professor Brian Tonner
Laboratory for Surface Studies
University of Wisconsin-Milwaukee
Milwaukee, WI 53201

Professor Joseph J. Fripiat
31 La Tuilerie
45240 Marcilly-en-Villette
France

Professor Menachem Steinberg
Dept. of Inorganic and Analytical Chemistry
The Hebrew University of Jerusalem
Jerusalem, Israel

Professor Michael Drechsler
CRMCC-CNRS
Université de'Aix-Marseille
Marseille, France

Professor Barney Webb
Materials Science Center
University of Wisconsin-Madison
Madison, WI 53706

One hundred and fifteen scientists from all parts of the U.S.A., from France, Germany, Israel, New Zealand, the People's Republic of China, and the United Kingdom participated. They came from universities (82%), from industry (14%), as well as government institutions (4%). The educational value of the conference is demonstrated by the fact that about 40% of the participants were Graduate Students and Post-Doctoral Fellows. The registration fee was kept as low as possible.

The following registration fees were requested:

Registration before 21 June 1985:

\$85.00 Regular

\$40.00 Graduate Students and Post-Doctoral Fellows

Registration after 21 June 1985:

\$105.00 Regular

\$ 50.00 Graduate Students and Post-Doctoral Fellows

Students in the UW-System paid a nominal fee.

Besides the scientific program, a number of social programs were arranged. They included dinner tours, a reception for speakers and participants from foreign countries, and a banquet. Many participants used the opportunity to visit the facilities of the Laboratory for Surface Studies at UWM. In connection with the Summer Institute, an exhibition of surface science books was organized.

International scientific societies and journals announced the conference. About 2700 scientists were contacted directly.

As in the case of former ISISS, the lecturers also wrote review papers which are published collectively in the form of a single volume book. Volume VI of "Chemistry and Physics of Solid Surfaces" is printed by Springer Verlag, Berlin-Heidelberg-New York-Tokyo.

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Dr. Ralf Vanselow
Director of ISISS

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